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A controlled fluorination method using elemental fluorine has been used to synthesize a large variety of new compounds from hydrogen-containing precursors including perfluoroethers, perfluoropolyethers, perfluoro crown ethers, and perfluorocryptands. Polyesters were converted to polyethers using a combination of direct fluorination of the carbon hydrogen bonds and fluorination by SF_4 of the carbonyl groups. A process was developed for partial fluorination of gas separation membranes. The selectivity of the membranes for size separation was increased significantly up to 10^3.

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CONTRACT/GRANT NUMBER: AFOSR-88-0084

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                          D. Wayne Dyer   Wen-Huey Lin
                          Brian Eastland   Todd Mlsna

PUBLICATIONS:*

"Synthesis of Unusual Perfluorocarbon Ethers and Amines Containing Bulky
Fluorocarbon Groups; New Biomedical Materials", H.N. Huang, D.F. Persico,
L.C. Clark, Jr. and R.J. Lagow, J. Org. Chem., 53, 78 (1988).

"Synthesis of Perfluoro Crown Ethers: A New Class of Cyclic Fluorocarbons",
W.H. Lin, W.I. Bailey, Jr. and R.J. Lagow, Pure Appl. Chem., 60, 473
(1988).

"The Preparation of New Perfluoro Ether Fluids Exhibiting Excellent Thermal
Oxidative Stabilities", W.R. Jones, Jr., T.R. Bierschenk, T.J. Juhlke, H.
Kawa and R.J. Lagow, Ind. Eng. Chem. Res., 27, 1497 (1988).

"Synthesis of the First Perfluoro Tetraalkyl Orthocarbonates", W.H. Lin,
W.D. Clark and R.J. Lagow, J. Org. Chem., 54, 1990 (1989).

"Synthesis of Bis(trifluoromethyl)xenon", L.J. Turbini, R.E. Aikman, M.M.
Brezinski and R.J. Lagow, J. Fluorine Chem., 45, 12 (1989).

"Synthesis of Tetrakis(trifluoromethyl)lead", T.J. Juhlke, J.I. Glanz and
R.J. Lagow, Inorg. Chem., 28, 980 (1989).

"The Synthesis of Perfluorodicyclohexyl-18-crown-6 Ether", T.Y. Lin and R.J. Lagow, J. Chem. Soc., Chem. Commun., 12 (1991).

"Synthesis of Functional Perfluorinated Resins, Branched Perfluorinated Ethers and Perfluoroalkanoyl Fluorides", H.N. Huang and R.J. Lagow, J. Chem. Soc., Perkin Trans. 1, 871 (1991).

"XPS Characterization of Surface Fluorinated Poly(4-methyl-1-pentene)", D.R. Paul, J.M. Mohr, Y. Taru, T.E. Mlsna and R.J. Lagow, J. Appl. Polym. Sci., 42, 2509 (1991).

"A New Synthetic Procedure for the Preparation and Manufacture of Perfluoropolyethers", T.R. Bierschenk, T.J. Juhlke, H. Kawa and R.J. Lagow, Synthetic Fluorine Chemistry, G.A. Olah, R.D. Chambers and G.K.S. Prakash, Eds., Wiley Interscience, in press.

"Selective Formation of Molecular Oxygen/Perfluoro Crown Ether and Perfluoro Cryptand Adduct Ions (Inclusion Complexes?) in the Gas Phase", J. Brodbelt, S.D. Maleknia, T.Y. Lin and R.J. Lagow, J. Am. Chem. Soc., in press.

"The Synthesis of Perfluorotrialkyl Orthoformates by Direct Fluorination", T.E. Mlsna, W.H. Lin, M.M. Hovsepian and R.J. Lagow, Eur. J. Solid State and Inorg. Chem., in press.

*Some of this work has been completed and published after the termination of this project on November 30, 1990.

ABSTRACTS OF OBJECTIVES AND ACCOMPLISHMENTS:

At a time when direct fluorination has been successfully scaled up by industrial concerns (3M and others) in conjunction with a small company composed of alumni from this AFOSR research program, our group continues to make novel contributions to the literature. During this three year period, we prepared the first perfluorocryptand (J. Org. Chem. 1990, 55, 5933). This perfluorocryptand [222] structure:
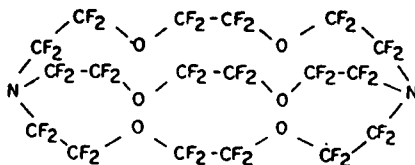
along with the perfluoro crown ethers (Pure Appl. Chem. 1988, 60, 473) have been ongoing projects in this laboratory. In a collaboration between our research group and the research group of Professor Jennifer Brodbelt we

"A New Trifluorosilyl Exchange Reagent: Reactions of Cd(SiF$_3$)$_2$·glyme with Dibromo Metal Phosphine Complexes of Platinum, Palladium, and Nickel Yield Trifluorosilyl Substituted Dialkyl Compounds", M.A. Guerra and R.J. Lagow, J. Chem. Soc., Chem. Commun., 65 (1990).

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"Synthesis of Tris(trifluoromethyl)gallium and Its Adducts", M.A. Guerra, D.W. Dyer, S.K. Mehrotra and R.J. Lagow, J. Organomet. Chem., 390, C73 (1990).

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"A New General Method for Preparation of Pentafluorosulfur-Substituted Fluorocarbons: The Synthesis of Perfluoroneopentyl Sulfur Pentafluoride Using Elemental Fluorine as a Reagent", H.N. Huang and R.J. Lagow, Chemistry of Materials, 2, 477 (1990).

"The Synthesis of the First Perfluorocryptand", W.D. Clark, T.Y. Lin, S.D. Maleknia and R.J. Lagow, J. Org. Chem., 55, 5933 (1990).

"The Synthesis of Highly Fluorinated Alkylcyclohexanes for Use as Oxygen Carriers; and the ^{19}F and ^{13}C NMR Spectra of Alkylcyclohexanes", W.H. Lin and R.J. Lagow, J. Fluorine Chem., 50, 345 (1990).

"A Facile Synthesis for Functional Perfluoropolyether Oligomers, Diacids, Diesters and Surfactants", D.F. Persico and R.J. Lagow, J. Polym. Sci., Polym. Chem. Ed., 29, 233 (1991).

"Novel Synthesis of Unusual Classes of Fluorocarbon Organosulfur Compounds Using Elemental Fluorine as a Reagent", H.N. Huang, H.W. Roesky and R.J. Lagow, Inorg. Chem., 30, 789 (1991).

"The Direct Fluorination of Acetone", W.D. Clark and R.J. Lagow, J. Fluorine Chem., 52, 37 (1991).

"Surface Fluorination of Composite Membranes Part I: Transport Properties", D.R. Paul, J.M. Mohr, T.E. Mlsna and R.J. Lagow, J. Membrane Science, 55, 131 (1991).

"Surface Fluorination of Composite Membranes Part II: Characterization of the Fluorinated Layer", D.R. Paul, J.M. Mohr, Y. Taru, T.E. Mlsna and R.J. Lagow, J. Membrane Science, 55, 149 (1991).

have recently shown that both perfluorocryptand and perfluoro crown ethers tenaciously bind O_2 and F (J. Am. Chem. Soc. 1991, in press). We have also generated several new classes of perfluoro crown ethers (J. Chem. Soc., Chem. Commun. 1991, 12). In addition, we have prepared many new spherical perfluorocarbon fluids based on pentaerythritol species as well as other types of spherical perfluorocarbon ethers. We have continued our work with Professor Leland Clark on strategically designed perfluorocarbon blood substitutes and established a general route to perfluorocarbon diacids and precursors for surfactants (J. Polym. Sci., Polym. Chem. Ed. 1991, 29, 233). Another contribution from our group has been the synthesis of some of the first sulfur pentafluoride substituted fluorocarbon polymers (J. Polym. Sci., Polym. Lett. Ed. 1990, 28, 297). Lower molecular weight versions have potential as high density fluids while solid samples and elastomers have potential new dielectric materials. We have also been working on new ^{19}F NMR magnetic resonance imaging agents. One of our best candidates is the perfluoro 15-crown-5 (J. Chem. Soc., Chem. Commun. 1985, 1350; U.S. Patent 4,570,005, 1986; U.S. Patent 4,838,274, 1989). Work has also continued on perfluoropolyether fluids. While our off-campus group has used the University of Texas technology in conjunction with Air Force Materials Laboratory at Wright-Patterson Air Force Base in developing some of the best and most stable nonflammable perfluorocarbon aircraft hydraulic fluid candidates available.

AFOSR Program Managers: Dr. Anthony Matuszko and Dr. Frederick Hedberg

Final Technical Report

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

Bolling Air Force Base, DC 20332

NEW EXPERIMENTAL CHALLENGES IN ELEMENTAL FLUORINE CHEMISTRY;

AN EMERGING TECHNOLOGY

Grant Number AFOSR-88-0084

December 1, 1987 - November 30, 1990

Presented by

Professor Richard J. Lagow

Department of Chemistry

The University of Texas at Austin

Austin, Texas 78712

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INTRODUCTION

This is a very exciting time for the chemistry of direct fluorination. For well over a decade our research group, funded by the Air Force Office of Scientific Research, has synthesized novel and unusual organofluorine compounds, many of which could not be prepared using other synthetic methods. Now this area of chemistry has come of age and one consequence is that there will be a much shorter lead time, perhaps significantly less than two years, elapse between the discovery of a potentially new or useful material in the laboratory and its availability on a commercial scale.

Just this July, 3M Company puts on line a new commercial production facility using our direct fluorination technology. A public announcement has been issued concerning 3M's licensing (which occurred secretly four years ago) of our perfluoroether and perfluoropolyether technology. That technology had its origin with our AFOSR funded projects. By the fall, the first round of commercial products will hit the market. Both Exfluor Research Corporation, an Austin corporation comprised primarily of a small group of former students from the Lagow laboratory, and 3M have now the capability of making many gallons per hour of interesting new fluorocarbons using elemental fluorine. The 3M technology package consisted of numerous patents produced by our group at the University of Texas along with a number of patents licensed from Exfluor Research Corporation.

Thus the work done in our laboratory has even greater impact since work done in the University laboratory (still on an eight to ten gram scale) can be converted in a relatively short period of time to very useful quantities of materials in any number of fields such as biomedical research, functional fluids and lubricants, surfactants and starting materials for new polymers and polymer systems.

Interestingly perfluoropolyether chemistry, one of the areas given our most attention in our academic laboratory over the last ten years and an area directly tied to the sponsorship of AFOSR, will constitute the lion's share of the first several waves of products to hit the market. Elemental fluorine perfluoroethers and the perfluoropolyether synthetic method came directly out of our AFOSR program with the first results reported in 1978.[1-3]

Thus our fluorocarbon program with AFOSR will most certainly develop as an outstanding example of funding basic research to achieve major impact on both the industrial and military sectors in the United States. In general, the Air Force Office of Scientific Research has been our sole support in exploring this area of chemistry and is certainly the only long term support for this elemental fluorine research program (several other agencies have picked specific narrow areas to support for lesser periods of time).

There are important new synthetic techniques emerging from our academic laboratory presently. In the next three years much more sophisticated work on more complex, higher molecular weight compounds will be possible. For example, Tzuhn-Yuan Lin, a very excellent new graduate student in our program, has been able to synthesize recently molecules such as the fluorocarbon analogue of the dibenzo crown ethers.
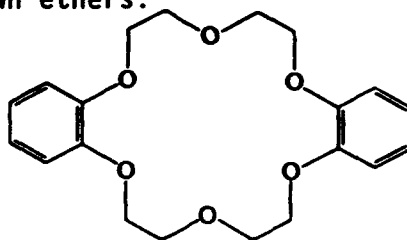

dibenzo(18)-crown-6

Tzuhn-Yuan Lin has prepared and we have recently submitted for publication in Chemical Communications two interesting isomers of perfluorodicyclohexyl-18-crown-6 ether, the cis-syn-cis and cis-anti-cis isomers.[4] Their structures have also been established by X-ray crystallography.
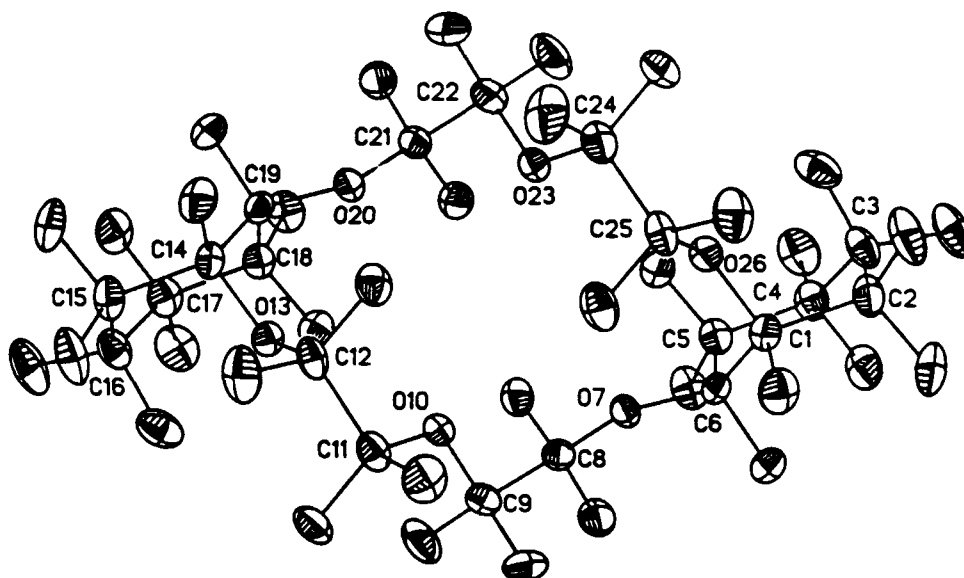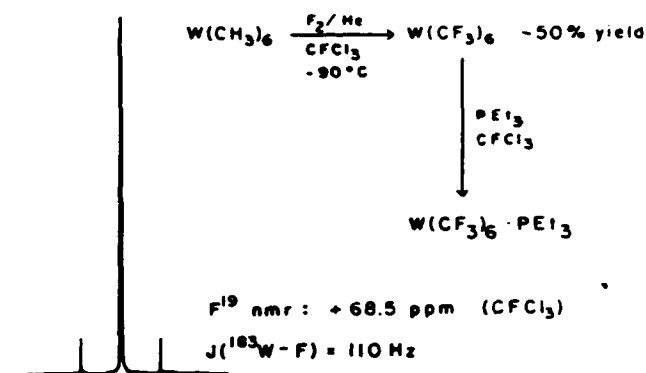
View (ORTEP) of *cis-syn-cis* (1) showing the atom numbering scheme. Distances (Å) between adjacent oxygen atoms are as follows: O_{13}–O_{20} 2.662, O_{20}–O_{23} 2.713, O_{23}–O_{26} 2.665, O_{26}–O_7 2.667, O_7–O_{10} 2.707, O_{10}–O_{13} 2.667. Distances (Å) between oxygen atoms to center of the molecule are follows: O_7 2.536, O_{10} 2.129, O_{13} 3.177, O_{20} 2.543, O_{23} 2.141, O_{26} 3.181.
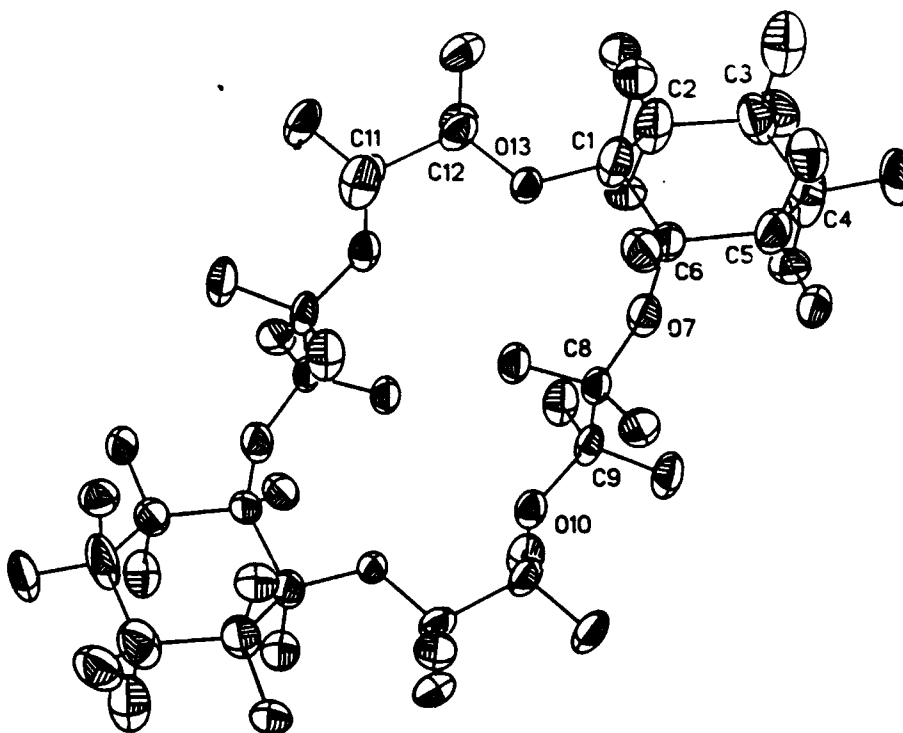
View (ORTEP) of *cis-anti-cis* (2) showing the atom numbering scheme. Distances (Å) between adjacent oxygen atoms are as follows: $O_{10'}$–O_{13} 2.727, O_{13}–O_7 2.702, O_7–O_{10} 3.525. Distances (Å) between oxygen atoms to center of the molecule are follows: O_7 3.156, O_{10} 2.403, O_{13} 3.332.

This is just an example of how well we can do with our direct fluorination technology at the present time. We expect that high molecular weight limitations will be nonexistent as we progress during the next three year period.

It is very significant that one of the new concepts enabling high volume production and scale-up of direct fluorination came from an experiment in our laboratory which was done several years ago, namely the synthesis of the perfluorinated analogue of Geoff Wilkinson's compound hexamethyltungsten by direct fluorination. It was very surprising that Robert Aikman, toward the end of his Ph.D. thesis, was able to convert hexamethyltungsten (containing a 20-30 kcal tungsten-carbon bond) to the fluorocarbon analogue in at least fifty percent yield.

$$W(CH_3)_6 \xrightarrow[\substack{CFCl_3 \\ -90°C}]{F_2/He} W(CF_3)_6 \quad \sim 50\% \text{ yield}$$

$$\downarrow \substack{PEt_3 \\ CFCl_3}$$

$$W(CF_3)_6 \cdot PEt_3$$

$$F^{19} \text{ nmr}: +68.5 \text{ ppm} \quad (CFCl_3)$$

$$J(^{183}W-F) = 110 \text{ Hz}$$

We have previously based our successful fluorinations on the philosophical approach developed by Lagow and Margrave and explained in <u>Progress in Inorganic Chemistry</u>[5] where direct fluorination was slowed down and carefully controlled by the supply of elemental fluorine as well as moderated with temperature control and other techniques like the Lagow cryogenic zone reactor.[5]

Thermodynamic Data for Steps in Fluorination of CH_4.[a]

Step		Reaction	$\Delta H_{298°K}$ kcal mole^{-1}	$\Delta H_{500°K}$ kcal mole^{-1}	$\Delta G_{298°K}$ kcal mole^{-1}	$\Delta G_{500°K}$ kcal mole^{-1}
Initiation	1a	$F_2 \rightarrow 2F\cdot$	+37.7	+38.5	+29.55	+20.9
	1b	$F_2 + RH \rightarrow R\cdot + HF + F\cdot$	+3.9	+5.1	-5.84	-18.904
Propagation	2a	$RH + F\cdot \rightarrow R\cdot + HF$	-33.8	-33.4	-36.215	-37.51
	2b	$R\cdot + F_2 \rightarrow RF + F\cdot$	-69.1	-69.5	-68.1	-64.15
Termination	3a	$R\cdot + F\cdot \rightarrow RF$	-106.8	-108.0	-97.5	-85.091
	3b	$R\cdot + R\cdot \rightarrow R-R$	-83.8	-83.06	-70.3	-57.5
Overall reaction		$R-H + F_2 \rightarrow RF + HF$	-102.9	-102.9	-103.4	-103.9

[a] Based on JANAF Table data for CH_4.

Fluorine dilution scheme direct fluorination.
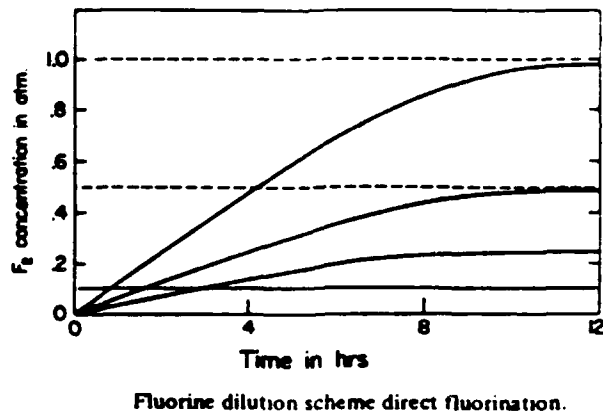
It was amazing that direct fluorination was capable in $CFCl_3$ at temperatures such as -90 °C was capable of preserving 20-30 kcal bonds when the overall reaction to replace even one hydrogen is over 100 kcal.

Most of our newer approaches, and there are more than one, are based on a new philosophy. Direct fluorination has many advantages for commercial and large-scale production as well as making large high molecular weight and sophisticated molecules for both kinetic and thermodynamic reasons. Although it was always expected, it has been established over the last ten years that reaction of elemental fluorine with hydrocarbons are perhaps the, or one of the, fastest reactions in all of chemical science.
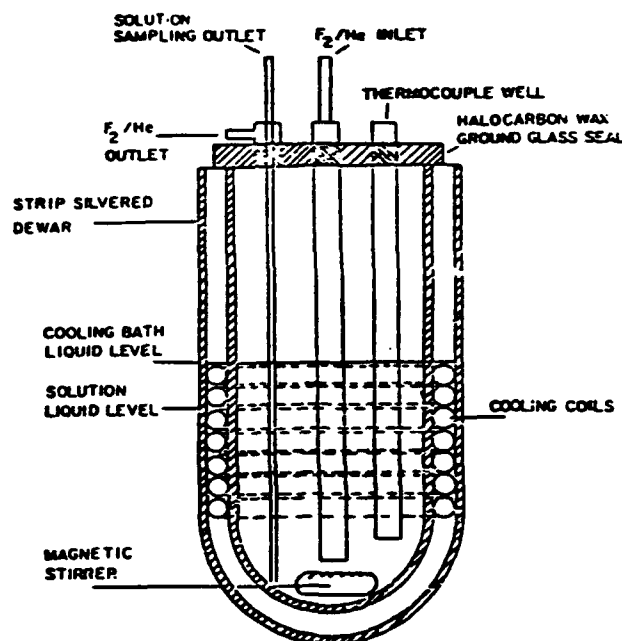
The activation energies for molecular fluorine to abstract a proton from an alkene has been reported in different studies to range from a real activation energy of zero to as high as 1 cal/mole (not 1 kcal/mole). These studies were reported by such researchers as Dick Bernstein of UCLA, Doug McDonald of the University of Illinois, and Dick Zare of Stanford. The exact number obtained for the activation energy depends on the method of measurement. A number of these results have come from crossed-beam reaction studies.

It has been known for some time, and is discussed in our Progress in Inorganic Chemistry article,[5] that the full substitution and replacement of protons on

hydrocarbons is among the most _exothermic_ reactions known. Thus if we neglect one small problem, namely control of the reactions of elemental fluorine, we are dealing with a reaction chemistry which has _unique_ advantages for chemical processing. There is, in principle, no limit to how fast these reactions with activation energies below 1 cal/mole can take place on an industrial scale. We also have a reaction whose thermodynamics are so favorable (exothermic) that the reaction proceeds _very far_ to the right and in fact can be quantitative in favorable instances. In most industrial chemistry processes, most of the primary obstacles are equilibrium problems. Successful chemistry often depends on catalysis or other methods for shifting equilibrium concentrations in the desired direction. Direct fluorination chemistry has essentially no equilibrium problem at all. Therefore industrial or academic scale reactions can be conducted very rapidly and efficiently, and in much higher yields than we ever thought possible.

With these advantages, the reaction chemistry we are dealing with has only one major problem. There is a need for a technique or system, perhaps involving a rapid heat sink, for removing energy from the reaction very rapidly. Essentially what we are describing is an _energy density_ problem. The vibrational relaxation must be rapid and efficient enough to keep the average energy density down after excited hydrocarbon free radicals are generated by reaction with fluorine molecules or fluorine atoms. The goal is that only the early (first through third) vibrational excited states of the molecules be populated and that these may be relaxed without ever entering the danger zone, namely the higher excited states close to the dissociation energy for a carbon-carbon bond or a carbon-fluorine bond.

It is known that cooled solvents are among the most efficient media for vibrational relaxation. One important technique involved the prototype low temperature solvent reactor developed in our laboratory for the $W(CF_3)_6$ synthesis.

SOLUTION SAMPLING OUTLET   F$_2$/He INLET

F$_2$/He OUTLET

THERMOCOUPLE WELL

HALOCARBON WAX GROUND GLASS SEAL

STRIP SILVERED DEWAR

COOLING BATH LIQUID LEVEL

SOLUTION LIQUID LEVEL

COOLING COILS

MAGNETIC STIRRER

Thus we predict that the chemical engineer of the future, after the full scale production capabilities of direct fluorination are well known and established, will say, "What I would really like is another reaction like direct fluorination to scale-up". He may have to search very far for one that is again so efficient. The solvent reactor is just one way to efficiently vibrationally relax the hydrocarbon species and we have developed techniques that control the reaction by both limiting the fluorine supply or by limiting the supply of hydrocarbon or other classes of reactants.

Professor Lagow and his former students have refined these processing techniques at Exfluor and since the patents are now issuing, we are reintroducing these into our academic laboratory. The result will be an increased capability of synthesizing exotic new species at the University of Texas plus much higher yields. The scale in the University laboratory will still be at the ten to fifteen gram level (up from one to two grams several years ago) for our mission in the University laboratory is to synthesize new and interesting molecules, not to do scaled-up chemistry.

To give an example of the impact, Dr. Hsu-Nan Huang, a former member of our laboratory now at Du Pont, had a working relationship with Leland Clark where he

supplied a gram or so of a new compound each month in exchange for physiological property data and oxygen solubility work. Thus we have a storehouse of knowledge on very interesting things and now that gallon scale can be provided off-campus, the academic work will have much higher impact in the oxygen carrier area. There is a whole lot of difference in the real world when there is one gram than when there is the potential for making many gallon quantities spurred by an important laboratory result. Here it should also be stated that even though direct fluorination can now be done in an industrial scale, considerable skill is required in the laboratory on prototype experiments directed toward preparation of new and unusual molecules. In fact it is still true that a new postdoctoral fellow, even well trained from another fluorine laboratory or a laboratory skilled in vacuum technology, will experience a five to six month period before being competitive on such reactions. Good graduate students sometimes require even longer to develop the "art of direct fluorination".

It should perhaps be stated that there are significant direct fluorination efforts underway as well at Du Pont, Monsanto, Air Products and Dow Chemical in the United States as well as a number of starts in projects in Japan. We think that the 3M effort with our group will lead the way and as this generates competition, we will need even more funding to compete and have impact in our academic laboratory as we deserve to still be in our own game. It should also be stated that there has been immediate Air Force impact in a number of areas. For example, Exfluor Research Corporation has a new 750 °F nonflammable hydraulic fluid on which initial testing at Wright-Patterson was so successful that 20 gallons were ordered from Exfluor recently for full-scale pump tests. 3M's new fluids will have impact on the military sectors as well as the microelectronics industry and many other areas of endeavor.

Another area where our research on perfluoropolyethers will have major impact is in the new Air Force Materials Laboratory initiative to make high temperature-high performance perfluoropolyether lubricants for advanced jet engines. Both 3M and
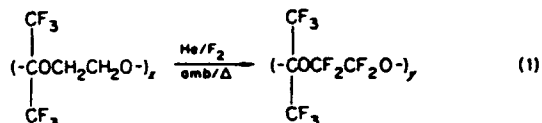
Exfluor stand to make major contributions based on chemistry arising originally from this AFOSR research program.

Our academic laboratory has been extraordinarily productive and successful under research grant AFOSR-88-0084 over the last four years. On pages 18-20 we list on contributions to the literature and it should be noted that we have 27 mainstream direct fluorination publications coupled with 11 publications in the trifluoromethyl organometallic area which we have also supported with our AFOSR funding bringing a total of 38 publications. We have many projects that are just turning the corner such as projects on new perfluorinated spiro compounds and new types of organometallic compounds as well as other totally new directions for the next three years. It should be noted that after intending to do so for a long time, we have finally launched a project into selective fluorination for this go around and have very promising results using lithium compounds, magnesium compounds, and boron compounds for precursors at low temperatures. This is a very different direction in our program.
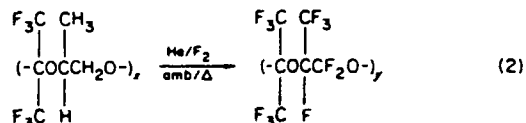
HIGHLIGHTS FROM OUR DIRECT FLUORINATION PROGRAM

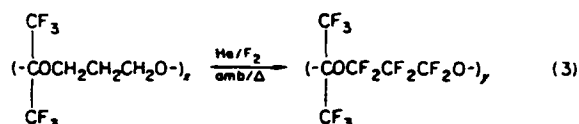We have made many new perfluoropolyethers[6] (Macromolecules 1985, _18_, 1383):

hexafluoroacetone/ethylene oxide copolymer

$$
\begin{array}{ccc}
CF_3 & & CF_3 \\
| & He/F_2 & | \\
(-COCH_2CH_2O-)_x & \xrightarrow{\text{amb}/\Delta} & (-COCF_2CF_2O-)_y \\
| & & | \\
CF_3 & & CF_3
\end{array}
\qquad (1)
$$

hexafluoroacetone/propylene oxide copolymer

$$
\begin{array}{ccc}
F_3C\ \ CH_3 & & F_3C\ \ CF_3 \\
|\ \ \ | & He/F_2 & |\ \ \ | \\
(-COCCH_2O-)_x & \xrightarrow{\text{amb}/\Delta} & (-COCCF_2O-)_y \\
|\ \ \ | & & |\ \ \ | \\
F_3C\ \ H & & F_3C\ \ F
\end{array}
\qquad (2)
$$

hexafluoroacetone/oxetane copolymer

$$
\begin{array}{ccc}
CF_3 & & CF_3 \\
| & He/F_2 & | \\
(-COCH_2CH_2CH_2O-)_x & \xrightarrow{\text{amb}/\Delta} & (-COCF_2CF_2CF_2O-)_y \\
| & & | \\
CF_3 & & CF_3
\end{array}
\qquad (3)
$$

We have developed a new method involving esters and SF_4 for fluorination of perfluoropolyesters and converting them using a second SF_4 step to obtain new perfluoropolyethers[7] (J. Am. Chem. Soc. 1985, _107_, 1197):

General Synthetic Scheme

$$
\begin{array}{c}
\text{(1)} \quad +OCR_aCOR'_b\}_n \ \xrightarrow[\text{amb}]{F_2/He} \ +OCR_fCOR'_f\}_n \\[2mm]
\text{(2)} \quad +OCR_fCOR'_f\}_n \ \xrightarrow[\text{amb}]{SF_4/HF} \ +OCR_fCOR'_f\}_n \\[2mm]
\text{(3)} \quad +OCR_fCOR'_f\}_{n_o} \ \xrightarrow[\text{T}\sim 70-150\,^\circ C]{F_2} \ +OCR_fCOR'_f\}_{n_f} \\[2mm]
n_o > n_f
\end{array}
$$
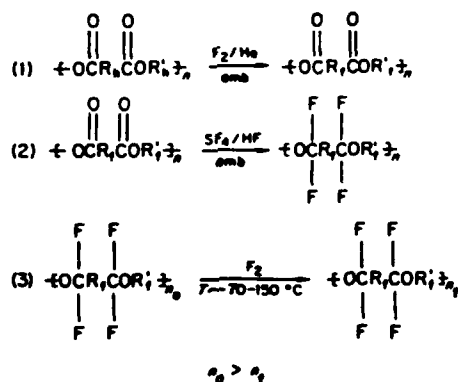
We have subsequently developed a method which is in press in J. Polym. Sci., Polym. Chem. Ed. to make functional perfluoropolyether oligomers, diacids, diesters and surfactants and starting materials for polymers using the same technology but using less than stoichiometric amounts of SF_4.[8]
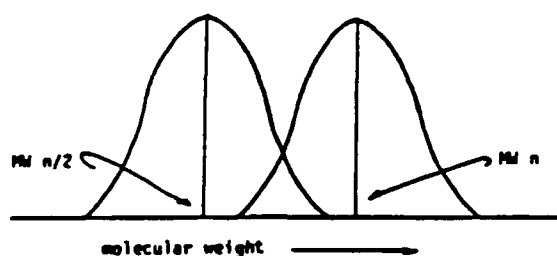
$$
\begin{array}{c}
O \qquad\qquad O \\
\| \qquad\qquad \| \\
HOCR_f OR'_f)_b COH
\end{array}
$$
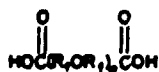
Figure 1. Gaussian distribution of difunctional perfluoropolyether molecular weights produced with n and $n/2$ mol of SF_4. Both samples are hydrolyzed to produce the diacids after treatment with SF_4.

SPECTRAL ASSIGNMENTS OF COMPOUNDS FROM 0% SF_4 REACTION

Compound	Highest m/e in mass spec	^{19}F NMR (rel. $CFCl_3$)	^1H NMR (rel. TMS)
$(CF_2CO_2CH_3)_2$	159 P-CO_2CH_3	-120.6	δ3.91
$(CO_2CH_3)_2$	59 P-CO_2CH_3		δ3.89
$(CF_2CO_2H)_2$	145 P-CO_2H	-120.3	δ11.43
$(CO_2H)_2$	45 P-CO_2H		δ9.00

SPECTRAL ASSIGNMENTS OF COMPOUNDS FROM 25% SF_4 REACTION

Compound	Highest m/e in mass spec	^{19}F NMR	^1H NMR
$(CF_2CO_2CH_3)_2$	159 P-CO_2CH_3	-120.6	δ3.96*
$(CO_2CH_3)_2$	59 P-CO_2CH_3		δ3.96*
$H_3CO_2CCF_2OCF_2CF_2CF_2CO_2CH_3$ a b c d	275 P-CO_2CH_3	a -77.8 b -83.7 c -126.8 d -119.1	δ3.96*

*Average chemical shift of CH_3's

SPECTRAL ASSIGNMENTS OF COMPOUNDS FROM 50% SF_4 REACTION

Compound	Highest m/e in mass spec	^{19}F NMR		^{1}H NMR
$H_3CO_2CCF_2OCF_2CF_2CF_2CO_2CH_3$ a b c d	275 P-CO_2CH_3	a	-77.3	63.93*
		b	-84.2	
		c	-127.0	
		d	-119.0	
$H_3CO_2CCF_2CF_2CF_2O(CF_2)_2OCF_2CF_2CF_2CO_2CH_3$ a b c d c b a	491 P-CO_2CH_3	a	-119.0	63.93*
		b	-127.0	
		c	-84.2	
		d	-88.7	
$H_3CO_2CCF_2OCF_2CF_2CF_2CF_2OCF_2CO_2CH_3$ a b c c b a	391 P-CO_2CH_3	a	-77.3	63.93*
		b	-84.2	
		c	-125.5	
$H_3CO_2CCF_2OCF_2CF_2CF_2CF_2OCF_2CF_2OCF_2CF_2CF_2CO_2CH_3$ a b c c b d d b e f	607 P-CO_2CH_3	a	-77.3	63.93*
		b	-84.2	
		c	-125.5	
		d	-88.7	
		e	-127.0	
		f	-119.0	

*Average chemical shift of CH_3's

SPECTRAL ASSIGNMENTS OF COMPOUNDS FROM 100% SF_4 REACTION

Compound	Highest m/e in mass spec	^{19}F NMR		^{1}H NMR
$(H_3CO_2CCF_2OCF_2CF_2CF_2CF_2OCF_2)_2$ a b c c b d	723 P-CO_2CH_3	a	-78.0	63.94*
		b	-83.3	
		c	-125.3	
		d	-88.6	
$(H_3CO_2CCF_2CF_2CF_2OCF_2CF_2OCF_2CF_2)_2$ a b c d d c e	823 P-CO_2CH_3	a	-119.3	63.94*
		b	-126.6	
		c	-83.3	
		d	-88.6	
		e	-125.3	
$H_3CO_2CCF_2O(CF_2CF_2CF_2CF_2OCF_2CF_2O)_2CF_2CF_2CF_2CO_2CH_3$ a b c c b d d b e f	939 P-CO_2CH_3	a	-78.0	63.94*
		b	-83.3	
		c	-125.3	
		d	-88.6	
		e	-126.6	
		f	-119.3	

*Average chemical shift of CH_3's

We have published a joint manuscript with Bill Jones of the Tribology Section of the National Aeronautics and Space Administration, Lewis Research Center entitled, "The Preparation of New Perfluoro Ether Fluids Exhibiting Excellent Thermal-Oxidative Stabilities"[9] (I&EC Research 1988, 27, 1497).

Viscosity Data

| compd | kinematic viscosity, cSt | | ASTM slope |
	38 °C (100 °F)	54 °C (130 °F)	
perfluorodiglyme	0.345	0.287	1.08
perfluorotetraglyme	0.802	0.631	1.01
perfluoro(1,3-diethoxypropane)	0.445	0.344	1.43
perfluoro(1,4-diethoxybutane)	0.610	0.440	1.61
HFPO hexamer	2.65	1.84	0.95
perfluoro(1,3-diethoxy-2,2-di-methylpropane)	0.707	0.557	1.04
perfluoro(penta-erythrityltetramethyl ether)	0.711	0.554	1.16

Thermal-Oxidative Investigation of Perfluoroalkyl Ethers

compd[a]	amt used, mg	dec. prod., mg	dec. after 48 h, %
perfluorotetraglyme	163	0.4	0.24
HFPO hexamer	188	0.4	0.22
perfluoro(1,3-diethoxypropane)	168	0.7	0.42
perfluoro(1,4-diethoxybutane)	234	1.1	0.48
perfluoro(1,3-diethoxy-2,2-di-methylpropane)	221	1.9	0.86
perfluoro(penta-erythrityltetramethyl ether)	195	2.5	1.28

[a] 100 Torr of O_2 (~25 °C) in each tube; test temperature, 360 °C; test duration, 48 h.

Another major breakthrough was the synthesis of the first perfluoro crown ethers[10,11] (J. Chem. Soc., Chem. Commun., 1985, 1350; J. Am. Chem. Soc., in press):

12-crown-4

perfluoro 12-crown-4

15-crown-5

perfluoro 15-crown-5

18-crown-6

perfluoro 18-crown-6
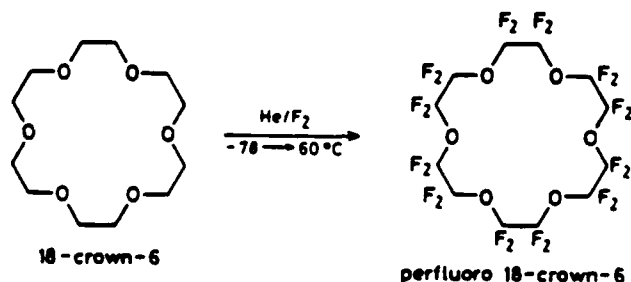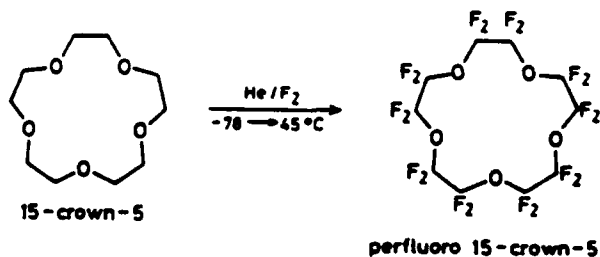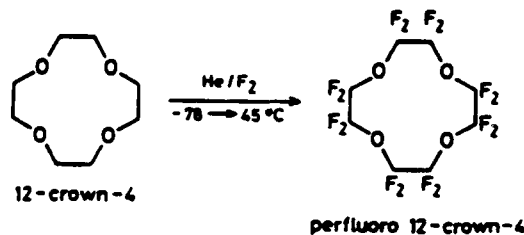
Properties and characterization of perfluoro 15-crown-5 and perfluoro 12-crown-4.[a] Satisfactory elemental analyses (C, F) were obtained.

	15-crown-5	12-crown-4
Boiling point, °C	146	118
I.r. (vapour phase), cm⁻¹	1250(s), 1228(vs), 1158(vs), 745(m)	1260(vs), 1188(vs), 1160(vs), 1080(m), 825(m), 745(br)
N.m.r. (neat liquid)	¹⁹F −91.8(s) p.p.m. (ext. CFCl₃) ¹³C δ 114.9 (s)	¹⁹F −90.0(s) p.p.m. (ext. CFCl₃) ¹³C δ 114.9 (s)
Mass spectrum, m/z	580 (C₁₀F₂₀O₅, M⁺)	445 (C₈F₁₅O₄, M⁺ − F)

[a] A table for the straight-chain fragmentation products listing mass spectral and ¹⁹F data (two pages) is available from the authors.

Additionally we have in press in the J. Org. Chem. a manuscript describing the first perfluorocryptand [222].[12]
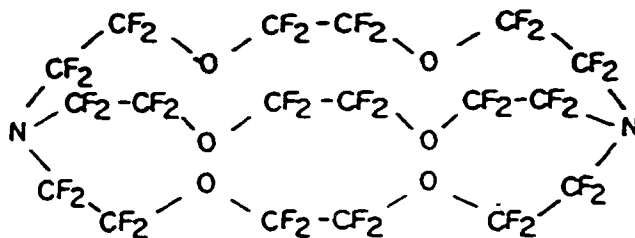

As will be later described, we have many other perfluoro macrocycle structures in mind. Dr. Hsu-Nan Huang, during his stay in graduate school, produced extraordinarily interesting new cyclic perfluorocarbons and highly branched perfluorocarbons with unusual properties[13] (Bull. Soc. Chim. Fr. 1986, 6, 993).
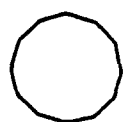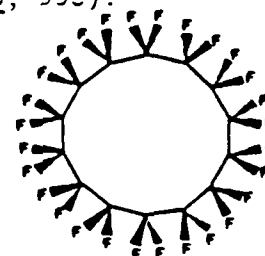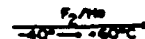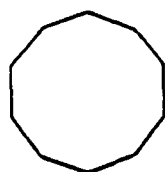

cyclododecane
m.p. 60°C
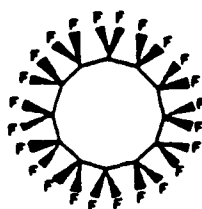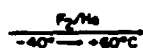
perfluorocyclododecane
b.p. 192 °C
m.p. -102 °C
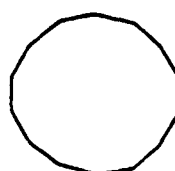
cyclotetradecane
m.p. 46°C

perfluorocyclotetradecane
m.p. 92° C
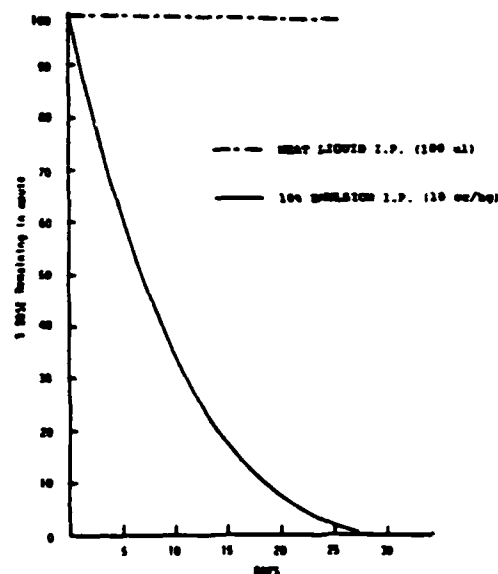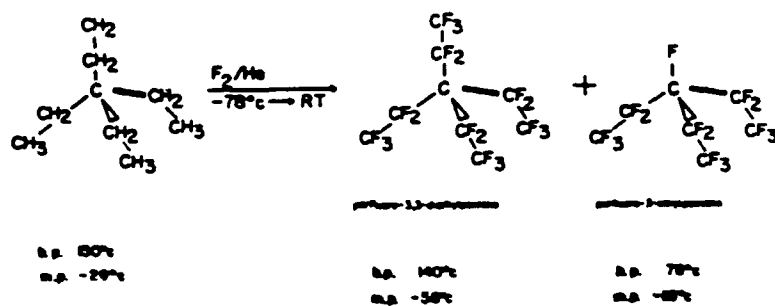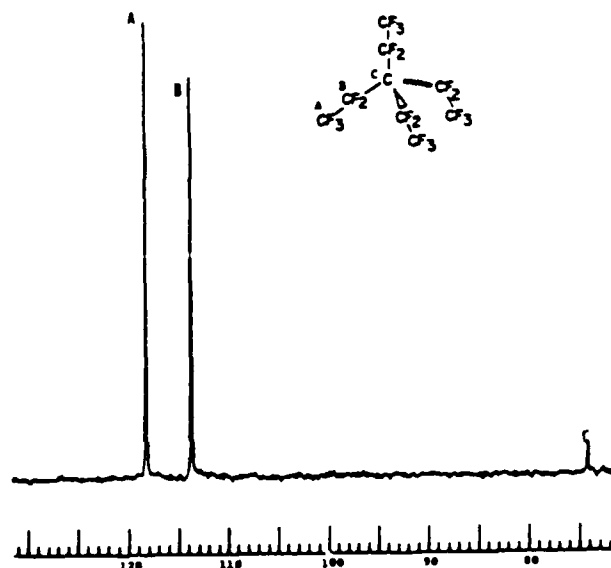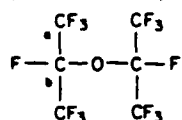
cyclodecane
b.p. 201°c
m.p. 9°c
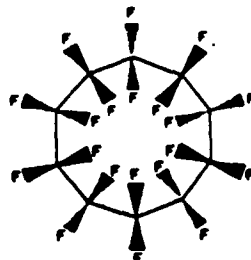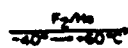
perfluorocyclodecane
b.p. 156°C
m.p. +13° C
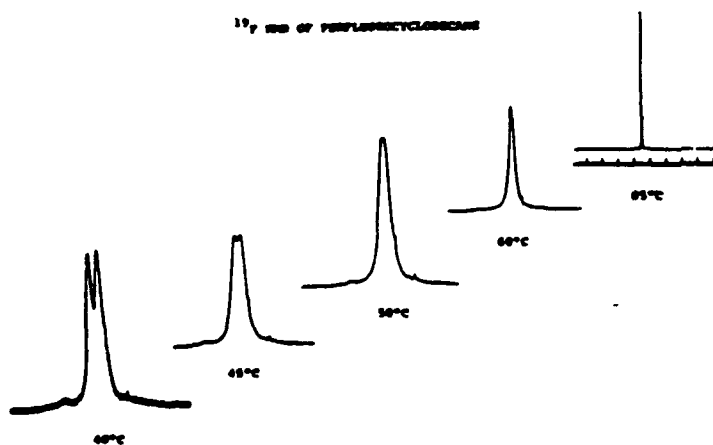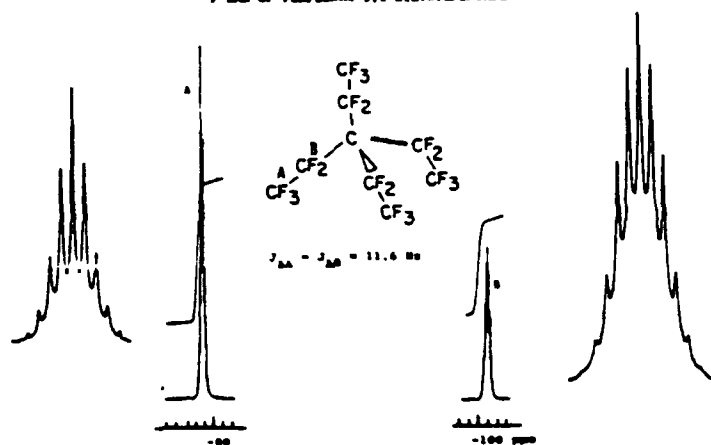
We have also had a strong component of our program directed toward new perfluoroethers of the small molecule variety[14,15] (J. Org. Chem. 1988, 53, 78; J. Org. Chem. 1985, 50, 5156).
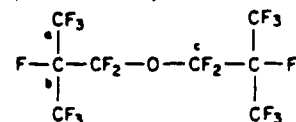
Chart I. $^{13}C\{^{19}F\}$ Assignments[a]
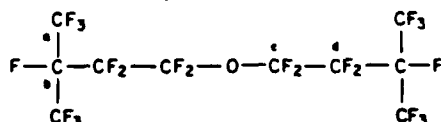
bis(perfluoroisopropyl) ether
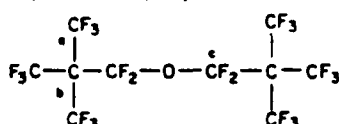

a 118.049
b 102.962

bis(perfluoroisobutyl) ether

a 118.960
b 88.980
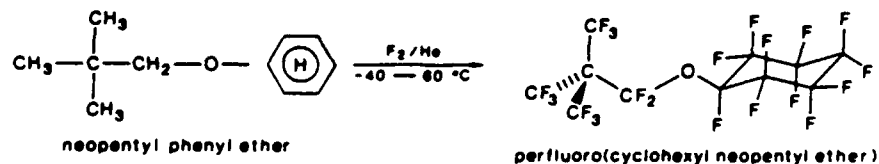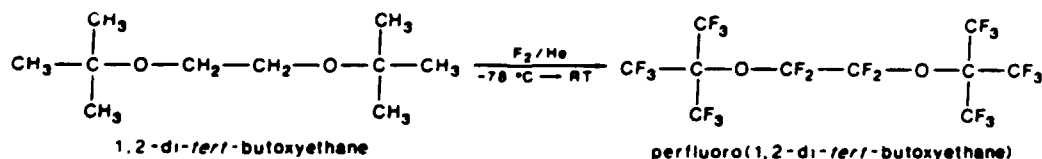c 117.659
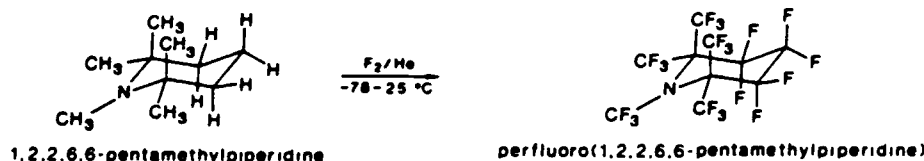
bis(perfluoroisopentyl) ether

a 119.285
b 90.215
c 116.684
d 110.831

bis(perfluoroneopentyl) ether

a 119.805
b 65.112
c 118.895

[a] In ppm relative to external Me$_4$Si.

(CH₃)₃COCH₃ → (CF₃)₃COCF₃ + (CF₃)₂CFCF₂OCF₃ + (CF₃)₃CF + (CF₃)₂CFCF₂H

conditions: −120 °C → RT, F₂/He

tert-butyl methyl ether

perfluoro(*tert*-butyl methyl ether)

perfluoro(isobutyl methyl ether)

perfluoro(2-methylpropane)

2-1-hydrononafluoro-2-methylpropane

2,2,5,5-tetramethyltetrahydrofuran → perfluoro(2,2,5,5-tetramethyltetrahydrofuran) + perfluoro(2,2,5-trimethyltetrahydrofuran) +

conditions: −120 °C → RT, F₂/He

3-hydropentadecafluoro-2,2,5,5-tetramethyltetrahydrofuran + perfluoro(2,2,5-trimethyltetrahydropyran)

tert-butyl isobutyl ether → perfluoro(*tert*-butyl isobutyl ether) + bis(perfluoroisobutyl) ether

conditions: F₂/He, −120 °C → RT

isopropyl ether → bis(perfluoroisopropyl) ether + perfluoro(isopropyl propyl ether) + perfluoro(ethyl isopropyl ether)

conditions: F₂/He, −120 °C → RT

2,5-dimethyltetrahydrofuran → perfluoro(2,5-dimethyltetrahydropyran)

conditions: F₂/He, −120 °C → RT

7-oxabicyclo[2.2.1]heptane → perfluoro(2-ethyltetrahydrofuran) + CF₃(CF₂)₃CF₃ perfluoropentane + perfluorohexanoyl fluoride

conditions: −120 °C → RT, F₂/He

1,2,2,6,6-pentamethylpiperidine → perfluoro(1,2,2,6,6-pentamethylpiperidine)

conditions: F₂/He, −78–25 °C

1,2-di-*tert*-butoxyethane → perfluoro(1,2-di-*tert*-butoxyethane)

conditions: F₂/He, −78 °C → RT

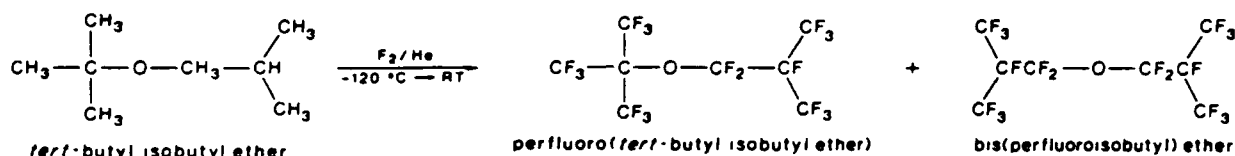neopentyl phenyl ether → perfluoro(cyclohexyl neopentyl ether)

conditions: F₂/He, −40–60 °C

Direct fluorination of perfluorocarbon ethers and amines.

We have a manuscript in press in J. Polym. Sci., Polym. Lett. Ed. on the synthesis of SF$_5$ substituted polymers II and III.[16]

$$(CH_2CH) \xrightarrow{\text{F}_2/\text{He}} (CH_2CH_2)_n$$
$$\quad | \qquad\qquad\qquad | $$
$$SCOBu^t \qquad\qquad SF_5$$
$$\quad \|$$
$$\quad O$$

$$\qquad I \qquad\qquad\qquad\qquad II$$

$$(CH_2CH_2)_n \xrightarrow{\text{F}_2/\text{He}} (CF_2CF_2)_n$$
$$\qquad | \qquad\qquad\qquad\qquad | $$
$$\qquad SF_5 \qquad\qquad\qquad SF_5$$
$$\qquad II \qquad\qquad\qquad\qquad III$$
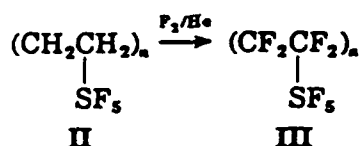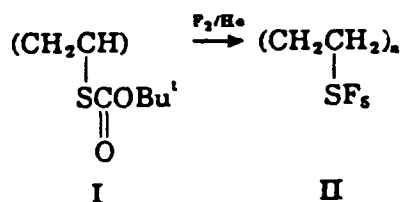
Another significant breakthrough that has been made in our laboratory is the process for partial fluorination of gas separation membranes. We have known from previous work that fluorination of polymer surfaces provides excellent gas diffusion barriers and liquid diffusion barriers. We reasoned that light fluorination of a selective gas separation membrane would change the selectivity in very pronounced ways. We have then tested this hypothesis on normal thin film membranes and soon hope to work on porous fiber (asymmetric) membranes. We have found that the selectivity increases especially for "size separation" systems are very large indeed (often after light fluorination the increase in selectivity is on the order of 10^3!). These observations according to Professor Don Paul, a recognized authority in the field, constitute a major breakthrough in separation technology. This area of chemistry will also be a substantial part of our new program; it is now being developed jointly with Professor Donald Paul of the University of Texas Department of Chemical Engineering. The first joint paper on this phenomenon was published in 1986.[17] We have presently three more manuscripts _in press_ from this collaboration.

Professor Richard J. Lagow

Recent Publications Arising from Air Force Office of Scientific Research

Grant AFOSR-88-0084

1. "The Synthesis of Perfluorinated Polyethers Via Polyesters Deriving From Hydrocarbons. A General Method," Makromol. Chem., Rapid Commun., 6, 85 (1985) (with D.F. Persico and G.E. Gerhardt).

2. "The Synthesis of Perfluoropolyethers Via Hydrocarbon Polyesters: A New General Method," J. Am. Chem. Soc., 107, 1197 (1985) (with D.F. Persico and G.E. Gerhardt).

3. "Synthesis of Branched Perfluoroethers By Direct Fluorination; Copolymers Based on Hexafluoroacetone," Macromolecules, 18, 1383 (1985) (with D.F. Persico).

4. "The First Perfluoro Crown Ethers," J. Chem. Soc., Chem. Commun., 19, 1350 (1985) (with W.H. Lin and W.I. Bailey, Jr.).

5. "Synthesis of New Cadmium Alkyls by Cocondensation of Cadmium Vapor with Trifluorosilyl and Trifluoromethyl Radicals," J. Chem. Soc., Chem. Commun., 1550 (1985) (with M.A. Guerra and T.R. Bierschenk).

6. "A General Synthesis for Symmetrical Highly Branched Perfluoroethers; A New Class of Oxygen Carriers," J. Org. Chem., 50, 5156 (1985) (with D.F. Persico, H.N. Huang and L.C. Clark, Jr.).

7. "The Generality of Metal Atom-Free Radical Reactions and Synthesis of New Trifluoromethyl Alkyls of Gold III and Silver," J. Organomet. Chem., 307, C58 (1986) (with M.A. Guerra and T.R. Bierschenk).

8. "Group IIB Metal Alkyls: The Synthesis and Stabilization of Trifluorosilyl and Trifluoromethyl Alkyls of Cadmium and Zinc," J. Am. Chem. Soc., 108, 4103 (1986) (with M.A. Guerra and T.R. Bierschenk).

9. "Gas Transport in Partially Fluorinating Low Density Polyethylene," J. Appl. Polym. Sci., 31, 2617 (1986) (with C.L. Kiplinger, D.F. Persico and D.R. Paul).

10. "Bis(trifluorosilyl)mercury, Bis(trifluoromethyl)mercury and Bis(trifluoro-methyl)tris(trimethylphosphine)nickel," Organometallic Syntheses, 3, 426 (1986) (with T.R. Bierschenk and W.I. Bailey, Jr.).

11. "High Yield Reactions of Elemental Fluorine," J. Fluorine Chem., 33, 321 (1986).

12. "Synthesis of New High Molecular Weight Cyclic Fluorocarbons and Highly Branched Fluorocarbons Such as Perfluoro-3,3-Diethylpentane," Bull. Soc. Chim. Fr., 6, 993 (1986) (with H.N. Huang).

13. "Further Developments of the Metal Vapor/Alkyl Radical Reaction. Synthesis of Tris(trifluoromethyl)indium and Bis(trifluorosilyl)cobalt and Their Base Adducts," Revue de Chimie Minerale, 23, 701 (1986) (with M.A. Guerra and T.R. Bierschenk).

14. "The Synthesis and X-ray Crystal Structures of $[Au(CH_2)_2PPh_2]_2(CF_3)_2$, $[Au(CH_2)_2PPh_2(C_6F_5)_2$ and $[PPN][Au(C_6F_5)_4]$: Two Dinuclear Gold(II) Ylide Complexes Containing Alkyl and Aryl Ligands and the First Example of a Homoleptic Au(III) Pentafluorophenyl Complex," Inorg. Chem., 26, 357 (1987) (with H.H. Murray, J.P. Fackler, Jr., L.C. Porter, D.A. Briggs and M.A. Guerra).

15. "Synthesis of Trifluorosilyl Organometallic Complexes From Trifluorosilyl Radicals and Metal Atoms," J. Am. Chem. Soc., 109, 4855 (1987) (with T.R. Bierschenk, M.A. Guerra, T.J. Juhlke and S.B. Larson).

16. "Synthesis of Unusual Perfluorocarbon Ethers and Amines Containing Bulky Fluorocarbon Groups; New Biomedical Materials," J. Org. Chem., 53, 78 (1988) (with H.N. Huang, D.F. Persico and L.C. Clark, Jr.).

17. "Synthesis of Perfluoro Crown Ethers: A New Class of Cyclic Fluorocarbons," Pure Appl. Chem., 60, 473 (1988) (with W.H. Lin and W.I. Bailey, Jr.).

18. "The Preparation of New Perfluoro Ether Fluids Exhibiting Excellent Thermal Oxidative Stabilities," Ind. Eng. Chem. Res., 27, 1497 (1988) (with W.R. Jones, Jr., T.R. Bierschenk, T.J. Juhlke and H. Kawa).

19. "Synthesis of the First Perfluoro Tetraalkyl Orthocarbonates," J. Org. Chem., 54, 1990 (1989) (with W.H. Lin and W.D. Clark).

20. "Synthesis of Bis(trifluoromethyl)xenon," J. Fluorine Chem., 45, 12 (1989) (with L.J. Turbini, R.E. Aikman and M.M. Brezinski).

21. "Synthesis of Tetrakis(trifluoromethyl)lead," Inorg. Chem., 28, 980 (1989) (with T.J. Juhlke and J.I. Glanz).

22. "A New Trifluorosilyl Exchange Reagent: Reactions of $Cd(SiF_3)_2 \cdot$glyme with Dibromo Metal Phosphine Complexes of Platinum, Palladium, and Nickel Yield Trifluorosilyl Substituted Dialkyl Compounds," J. Chem. Soc., Chem. Commun., 65 (1990) (with M.A. Guerra).

23. "A Synthesis for SF_5 Substituted Fluorocarbon Polymers," J. Polym. Sci., Polym. Lett. Ed., 28, 297 (1990) (with H. Kawa, S.N. Partovi and B.J. Ziegler).

24. "Synthesis of Tris(trifluoromethyl)gallium and Its Adducts," J. Organomet. Chem., 390, C73 (1990) (with M.A. Guerra, D.W. Dyer and S.K. Mehrotra).

25. "The Synthesis of Perfluoro Highly Branched Heterocyclic Fluorine Compounds by Direct Fluorination," J. Fluorine Chem., 50, 15 (1990) (with W.H. Lin).

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